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Electrochemical behavior of Mg electrode in sodium salt electrolyte system

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A suitable electrolyte is crucial to enhancing the electrochemical performance of magnesium (Mg) batteries. Here, the influence of Na₂SiO₃ on the electrochemical behavior of AZ31B Mg alloy in the Na₂SO₄-NaNO₃ composite electrolyte was investigated. The results revealed that the activation potential of the AZ31B Mg alloy first represented a negative shift and then a positive shift with the increase in Na₂SiO₃. The most negative activation potential (−1.51 V) and the lowest polarization (−3.20 V) were found when 6 mM of Na₂SiO₃ was added; no discharge hysteresis was observed, and the polarization resistance value (R_1) was 3,806 Ω. After 24 h immersion in the composite electrolyte with Na₂SiO₃, more and wider cracks appeared on the alloy surface, where a thick, dense film was formed, showing excellent discharge performance and corrosion resistance.

KEYWORDS

AZ31B Mg alloy, composite electrolyte, Na₂SiO₃, electrochemical performance, corrosion behavior

Introduction

In view of the limited nature and high price of lithium resources, the research on electrochemical energy storage devices, such as non-lithium batteries (Zhang J. L. et al., 2021; Liu et al., 2021; Wan et al., 2022) and supercapacitors (Zhang Y. et al., 2021; Wei et al., 2021) is increasing. Magnesium (Mg) holds a promising application in anode materials for the first-generation Mg battery owing to its abundance, small density (1.74 g cm^{−3}), low cost, and excellent electrical conductivity (Bertasi et al., 2016; Yang et al., 2022). In addition, located on the diagonal of the periodic table, Mg and Li share many similar chemical properties. The standard electrode potential of metallic Mg is −2.36 V (vs. SHE), allowing the formation of large open-circuit voltage and working voltage (Deng et al., 2019; Maddegalla et al., 2021). Mg has an electrochemical equivalent of 0.454 g Ah^{−1} and a theoretical specific capacity up to 2,202 mAh g^{−1}, enabling it to be applied to long-time discharge (Kékedy-Nagy et al., 2021). However, shortcomings also remain unresolved, such as the lessened battery storage capacity after discharge, voltage hysteresis, severe inferior corrosion resistance of the electrode, and poor current efficiency, forming the main obstructors of the commercial availability of Mg battery (Shao et al., 2015; Horia et al., 2022; Zhang et al., 2022). In the Mg battery, “voltage lag” is the essence of the passivation of the Mg electrode in the electrolyte. Passivation film hinders the reaction during battery discharge, and its breakdown promotes a smooth reaction. Therefore, a

Mg battery is required for the normal voltage output over a period of time. The “hysteresis” in the Mg battery is mainly relevant to the coverage degree of surface passivation film and the rate and relaxation time of film breakdown (Gong et al., 2022; Wei et al., 2022).

Recently, employing a suitable additive into electrolytes has been proved to be simple and effective in changing the surface membrane structure of the Mg electrode, thus reducing voltage lag (Li et al., 2021). The presence of both 0.005 M EDTA-ZnNa₂ and 0.01 M C₆H₁₁NaO₇ has been demonstrated to remarkably inhibit corrosion and improve the performance of Mg battery for pure Mg in 3.5 wt% NaCl electrolyte (Qu et al., 2022). Zhao et al. (2016) investigated the discharge performance of an oxyanion corrosion inhibitor (Li₂CrO₄) as an electrolyte additive in 3.5 wt% NaCl electrolyte for Mg-air battery, verifying enormously reduced corrosion current density of AZ31B Mg alloys in the presence of 0.1 wt% Li₂CrO₄, which is beneficial to the intermittent discharge performance of the Mg-air battery.

Sodium metasilicate (Na₂SiO₃) is relatively cheap, environment-friendly, and non-toxic, often used as an anionic corrosion inhibitor (Kong et al., 2022). This thesis mainly explored the electrochemical performance and corrosion behavior of AZ31B Mg alloy in Na₂SO₄-NaNO₃ and Na₂SiO₃ composite electrolyte to pick out the matching electrolyte, thus ensuring the activation of the electrode and inhibiting the hydrogen evolution-induced self-corrosion.

Experiment

Chemicals and materials

In this study, Na₂SO₄, NaNO₃, and Na₂SiO₃ of analytical grade (≥99%) were utilized. The electrolyte was obtained by a mixture of 2 M Na₂SO₄ and 2 M NaNO₃ (volume ratio = 1:9), and the Na₂SiO₃ concentration ranged from 0.2 to 1.0 mM.

According to our previous work (Xu et al., 2017), the AZ31B Mg alloy (3.0 wt% Al, 1.0 wt% Zn, 0.2 wt% Mn, and 96.8 wt% Mg) was purchased from Wuxi Xinbiao Metal Material Co. Ltd. in China. The Mg alloy was sheared into an appropriate size of 1 × 1 cm with a thickness of 0.6 cm, then embedded with electric conductive copper wire, and encapsulated with epoxy resin in quick succession. Subsequently, these prepared samples were used as the working electrode for the electrochemical analysis.

Electrochemical characterization

The electrochemical characterization was performed on an electrochemical measurement system (CHI660E, China) using a standard three-electrode system comprising the graphite rod as the counter electrode, the saturated calomel electrode as the reference electrode, and the AZ31B Mg alloy as the working electrode.

The influence of Na₂SiO₃ additive on the electrochemical behavior of AZ31B Mg alloy electrode in the Na₂SO₄-NaNO₃ composite

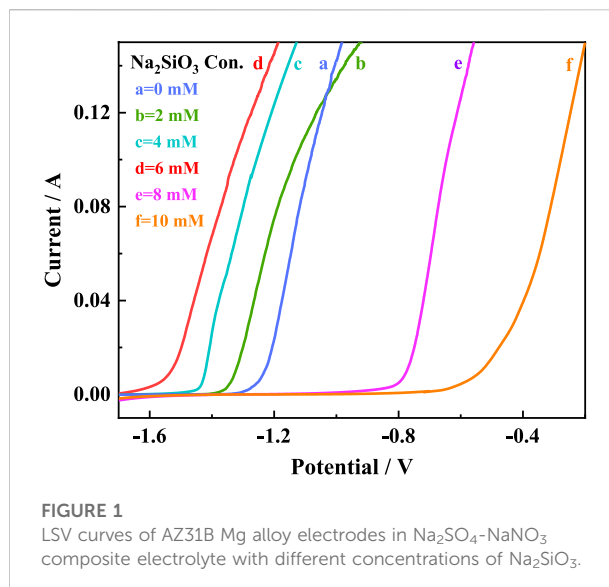


FIGURE 1
LSV curves of AZ31B Mg alloy electrodes in Na₂SO₄-NaNO₃ composite electrolyte with different concentrations of Na₂SiO₃.

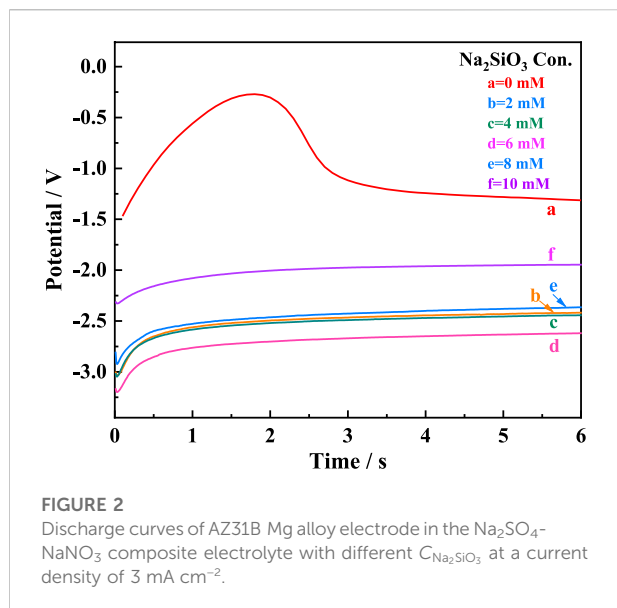
electrolyte was investigated by the linear sweep voltammetry (LSV) at a sweep rate of 1 mV s⁻¹. The discharge curves were explored at a discharge current density of 3 mA cm⁻². Moreover, the electrochemical impedance spectroscopy (EIS) was conducted at open circuit potentials in the range of 10⁻²~10⁵ Hz with an amplitude of 5 mV.

Surface morphology analysis

The effect of the Na₂SiO₃ additive on the morphology of the corrosive film layer on the Mg alloy electrode surface immersed into the Na₂SO₄-NaNO₃ composite electrolyte with or without Na₂SiO₃ (0.6 mM) for 24 h was revealed by the scanning electron microscopy (SEM, HITACHI S 4800) at an operating voltage of 15 kV.

Results and discussion

The AZ31B Mg alloy electrodes were soaked in the Na₂SO₄-NaNO₃ composite electrolytes of different Na₂SiO₃ concentrations (C_{Na₂SiO₃}) for 24 h. Then, the LSV curves of the electrodes were measured at a sweep rate of 1 mV s⁻¹, and the results are shown in Figure 1. The inflection point on the curve is generally referred as the activation electrode potential (E_{act}). Generally, negative values of E_{act} imply a low self-corrosion rate and a high discharge activity, under which the Mg alloy is strongly corrosion-resistant (Wang et al., 2014). Based on the curves, Na₂SiO₃ addition led to negative shifts in E_{act}, indicating the ability of Na₂SiO₃ to improve the discharge behavior of the Mg alloy electrode in the composite electrolyte. With the increase in C_{Na₂SiO₃}, E_{act} values shifted negative first and then positive. E_{act} reached to lowest point (-1.51 V) when C_{Na₂SiO₃} was 6 mM, 1.1 V poorer than the original value without Na₂SiO₃ additive. A plausible reason was that the Na₂SiO₃ addition affected the ionization

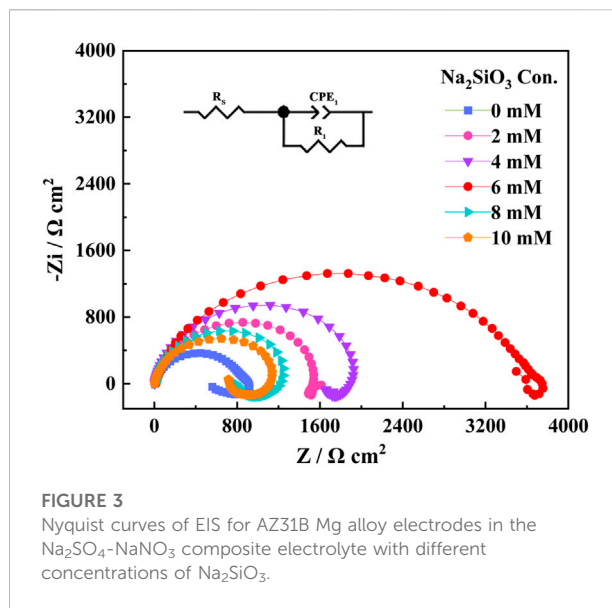


equilibrium by accelerating the release of Mg²⁺ ions from the Mg alloy, consequently improving the ionic conductivity and the mass transfer of Mg²⁺ ions (Zhang et al., 2022). The shift of E_{act} values might also be closely related to the microstructural change of the Mg alloy in the composite electrolyte added with Na₂SiO₃, as verified by the SEM images (vide infra).

Figure 2 illustrates the discharge curves of AZ31B Mg alloy electrodes in the composite electrolytes with varying C_{Na₂SiO₃} at a discharge current density of 3 mA cm⁻². In the absence of Na₂SiO₃, the discharge potential reached its maximum rapidly at the initial discharge stage and then slowly recovered to a stable state, which was ascribed to the activation process. This period lasted for 2.7 s and was attributed to the “hysteresis time.” Surprisingly, the “hysteresis time” disappeared after the addition of Na₂SiO₃, and the discharge curves were rapidly stabilized. Na₂SiO₃, as a type of surfactant, loosened the passive film on the electrode surface, promoting detachment and hence eliminating the hysteresis time required for the current to penetrate the passive film and enhancing the discharge activity of Mg alloy electrodes.

Notably, the Na₂SiO₃ addition reduced the discharge potential, which was -1.93 V in the composite electrolyte without Na₂SiO₃ at 3 mA cm⁻². In particular, when C_{Na₂SiO₃} was 6 mM, the discharge voltage occurred at -3.21 V, corresponding to a negative shift of 1,380 mV. This facilitated the increase in the output voltage of a battery cell. However, the discharge potential shifted positively with C_{Na₂SiO₃} > 6 mM. It is speculated that at high Na₂SiO₃ concentrations, the excess SiO₃²⁻ ions may react with Mg²⁺ ions in the electrolyte to form deposits on the electrode surface (Ge et al., 2013), potentially thickening the passive film on the electrode surface and hindering the discharge of the electrode, thus shifting the discharge potential to the positive direction.

The EIS spectra of the AZ31B Mg alloy electrodes after 24 h immersion in the composite electrolytes of varying Na₂SiO₃ concentrations are shown in Figure 3. EIS was conducted at an



open-circuit potential of 10⁻²~10⁵ Hz, with a sinusoidal disturbance amplitude of 5 mV. The insert illustrated the equivalent circuit of the EIS system. In the equivalent circuit diagram, R_s was induced by the solution resistance; 下标 corresponded to the high-frequency charge-transfer resistance arising from the alloy surface and corrosive film layer. CPE₁ denoted the double-layer capacitance induced by irregular oxide film on the alloy surface.

As shown in Figure 3, the EIS plots exhibited capacitive loops of similar shapes at low and high frequencies, and only some changes took place in the radii of the capacitive loops, indicating that the corrosion mechanism of the AZ31B Mg alloy was free from the influence of the addition amount of Na₂SiO₃. At a Na₂SiO₃ concentration of 6 mM, the capacitive reactance diameter reached the maximum. According to the curves, R₁ was 957 Ω in the absence of Na₂SiO₃. With the Na₂SiO₃ addition, the resistance value was enhanced significantly, indicating the prohibited corrosion of the AZ31B Mg alloy in the Na₂SO₄-NaNO₃ composite electrolyte. When C_{Na₂SiO₃} was 6 mM, the R₁ value reached the maximum of 3,886 Ω, increasing by more than four times and representing a stronger corrosion resistance.

The surface morphology images of AZ31B Mg alloy electrodes after 24 h immersion in the Na₂SO₄-NaNO₃ composite electrolyte are shown in Figure 4. Figures 4A,B show the SEM images of electrodes soaked in the absence of Na₂SiO₃. After 24 h of soaking, a thick, dense, and smooth film was formed on the Mg alloy electrode. Despite their large number, the cracks appearing on the surface were very narrow (generally <3 μm in width). As a result of hydrogen evolution from the electrode during the early soaking stages, a few small holes and pits were formed on the film. After 24 h of soaking in the presence of 6 mM Na₂SiO₃ (Figures 4C,D), the alloy surface exhibited more and wider cracks (the widest cracks exceeded 10 μm in width). A thick and dense film was formed, effectively protecting the Mg alloy electrode and enhancing its corrosion resistance.

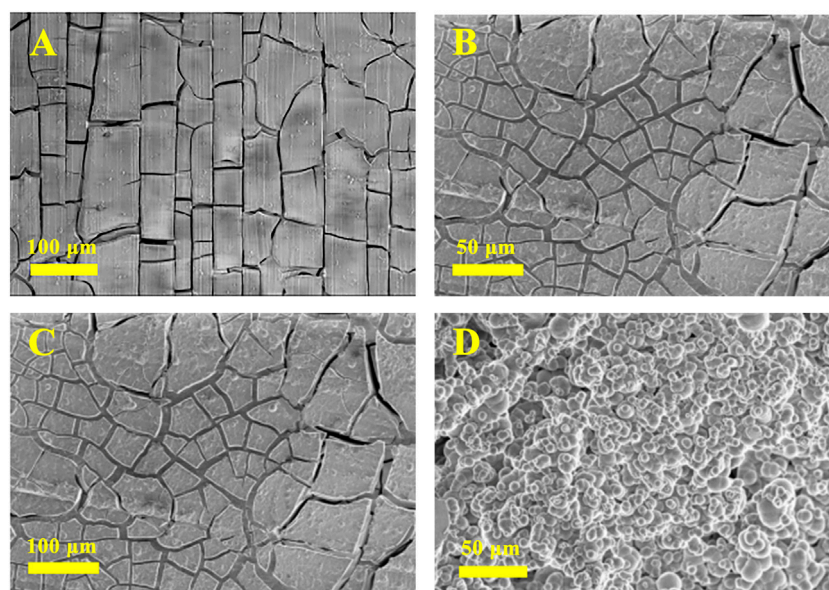


FIGURE 4
SEM of the AZ31B Mg alloy soaked in the Na_2SO_4 - NaNO_3 composite electrolyte in the absence (A,B) and presence (C,D) of Na_2SiO_3 for 24 h.

Conclusion

The influence of Na_2SiO_3 on the electrochemical and corrosion behavior of the AZ31B Mg alloy electrode in the Na_2SO_4 - NaNO_3 composite electrolyte (the volume ratio of 2 M Na_2SO_4 to 2 M NaNO_3 was 1:9) was investigated in this work. When $C_{\text{Na}_2\text{SiO}_3}$ was 6 mM, E_{act} values reached -1.51 V, 1.1 V lower than that without the Na_2SiO_3 additive. In particular, the discharge voltage occurred at -3.21 V, shifting negative to 957 mV, and the discharge curves were rapidly stabilized. Moreover, the resistance value reached a maximum value of 3,886 Ω , increasing by more than four times. The composite electrolyte with 6 mM Na_2SiO_3 was appropriate for Mg alloy, loosening the passive film on the electrode surface, facilitating the ionic conductivity, and eliminating the hysteresis time. This can realize not only the excellent discharge activity but also the high corrosion resistance of Mg alloy electrodes. Therefore, the present work offers a new electrolyte formulation to enhance the electrochemical behavior and lifespan of Mg batteries.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors without undue reservation.

Author contributions

YZ: Data curation, Investigation, Writing-original draft. QZ: Data curation, Investigation. CS: Writing-review and editing. CL: Project administration, Linguistic modification.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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